

FUTURE DIRECTIONS OF X-RAY MICROANALYSIS IN THE
ANALYTICAL ELECTRON MICROSCOPE

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INTRODUCTION

In the last 20 years, the analytical electron microscope (AEM) has allowed investigators to obtain chemical and structural information from < 100 nm diameter regions in thin samples of materials. The increased spatial resolution of the instrument and micro-chemical analysis capability has allowed investigators to explore problems where reactions occur at boundaries and interfaces or within small particles or phases in bulk samples. This paper discusses the future directions for micro-chemical analysis using x-ray spectroscopy.

X-RAY SPATIAL RESOLUTION - MINIMUM DETECTABILITY LIMIT

The spatial resolution of x-ray microanalysis in a thin foil is determined by the size of the beam specimen interaction volume. This volume is a combination of the incident electron beam diameter, d , and the beam broadening, b , due to elastic scatter within the specimen. Definitions of spatial resolution have been proposed by several authors (Goldstein, et al., 1977, Reed, 1982 and Michael, et al., 1990). For the average size of the interaction volume R , midway through the thin foil (Figure 1), $R = [d + (d^2 + b^2)^{1/2}] / 2$. This definition ignores the effects of diffraction and fast secondary (FS) electrons. Recent Monte Carlo calculations show that FS are only significant for elements below atomic number 13 (Al), (Williams, et al., 1991, 1992). High brightness guns, such as a field emission gun (FEG), produce the smallest sized probe diameters for the same beam current and x-ray generation in the sample and provide for the highest spatial resolution as long as beam broadening is not a dominant factor.

The minimum mass fraction (MMF) represents the smallest concentration of an element that can be measured in the analysis volume as defined by the spatial resolution, R . The MMF can be improved by increasing the current in the focused probe, increasing the electron beam energy to increase peak to background, P/B , and by increasing the analysis time. Currently MMF values of 0.1 to 0.2 wt% can be achieved using an EDS detector.

The x-ray spatial resolution, R , and the MMF are not independent of one another (Goldstein et al, 1990). The trade off between spatial resolution and MMF is shown in Figure 2 for measurements of Ni in an Fe-25 wt% Ni alloy (Goldstein, et al., 1990). The spatial resolution, R , approaches the beam diameter, d , in the thinnest specimens. The usefulness of the FEG is clearly illustrated in Figure 2 where spatial resolution, R , can be improved by almost an order of magnitude from ~ 15 to ~ 1.8 nm for the same MMF and electron beam energy (100 keV). The MMF decreases (improves) continuously as the specimen thickness and spatial resolution increases. It is unlikely that MMF will be better than 0.1 wt%, when using an EDS detector, no matter how large the analysis volume. This limitation is caused by the inability of the EDS detector to accept x-ray count rates which give dead times above ~ 20%. The best compromise in terms of improving x-ray spatial resolution and MMF is to use high operating voltages (300 to 400 kV), a FEG instrument, and thin specimens.

Of interest is the ultimate ability of the AEM to detect the presence of only a few atoms in the analysis volume. For an Fe-Ni alloy analyzed in a VG HB501 FEG AEM operating at 100 keV, with a spatial resolution of 2.5 nm (FWTM), a foil thickness of 20 nm, a counting time of 120 s and a MMF of 0.4 wt% Ni using an EDS detector, ~ 350 atoms of an element of interest are detected in the analysis volume. If the counting time is increased by a factor of 10 using a more stable sample stage and instrument electronics and if the operating voltage is increased to 300 kV, and the foil thickness reduced to 10 nm, the spatial resolution would improve to ~ 1.5 nm (FWTM) and the MMF would improve to ~ 0.1 wt %. In this situation, ~ 1 to 2 atoms of an element of interest could be detected in the analysis volume. With expected improvements in AEM instrumentation to reduce background and to improve peak to background and in improvements in

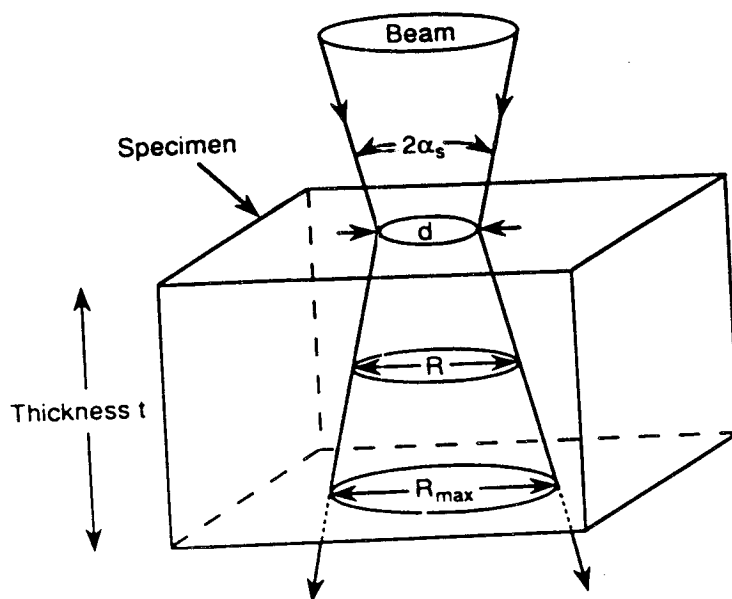


Figure 1. Definition of spatial resolution R in thin foil microanalysis (Goldstein et al., 1990). (Older but commonly used value for spatial resolution in microanalysis is R_{\max}).

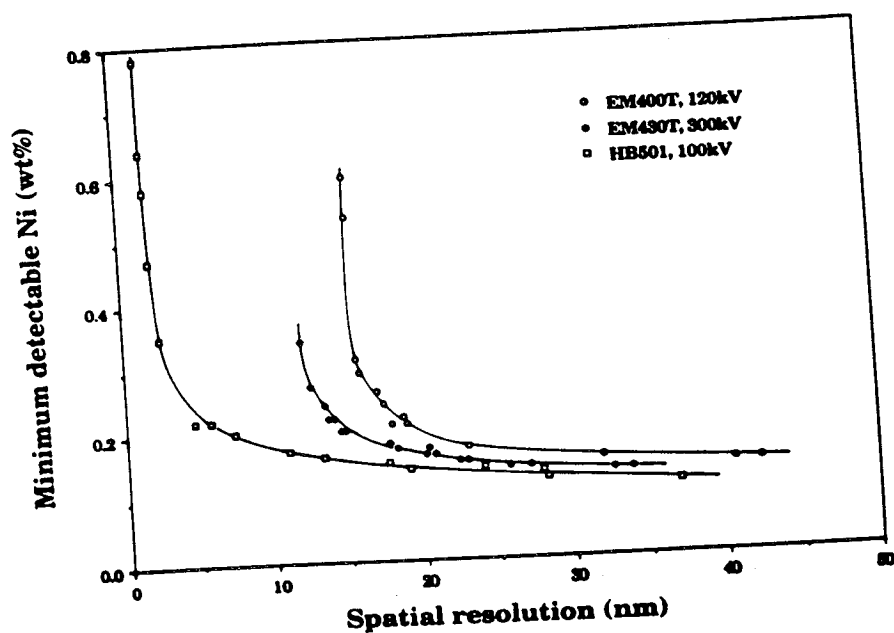


Figure 2. Relationship of spatial resolution and MMF measured for Ni in Fe-25 wt% Ni alloy by three AEM instruments (Goldstein et al., 1990). Operating conditions are 1) Philips EM400T: 120 kV, LaB₆ gun, spot size 4, 0.09 nA beam current, 15.5 nm probe diameter (FWTM), 2) Philips EM430T: 300 kV, LaB₆ gun, spot size 4, 0.26 nA beam current, 11.8 nm probe diameter (FWTM), 3) VG HB501: 100 kV, FEG, 0.3 to 0.35 nA beam current, 1.8 nm probe diameter (FWTM). Counting time, 120 s.

the preparation of thin-foils, it will be possible to detect the presence of single atoms in the analysis volume.

SPECIMEN PREPARATION AND CLEAN ROOM TECHNIQUE

To improve spatial resolution and MMF to the single atom analysis region, one must obtain thin foil samples approaching 10 nm in thickness. The two major methods, jet electropolishing and ion beam thinning, subject the thin regions of the sample to either severe mechanical stress combined with rapid electro-chemical dissolution or intense ion-beam heating, differential sputtering and surface damage. As discussed by Williams and Goldstein (1991), there is ample evidence that both electropolishing and ion-beam thinning can change the surface chemistry and introduce severe heating effects. It is critical, however, that the thin foils continue to have the same composition and other characteristics of the bulk sample.

To handle the thin specimens required for high spatial resolution microanalysis, more careful specimen handling techniques will need to be developed. Typical clean room techniques will be adopted so that specimens and sample holders are cleaned and handled in laminar flow hoods. More often than not specimens will have to be heated using infrared techniques to remove water and residual hydrocarbon films from prior thinning as well as "dusted off" in an ultra high vacuum specimen preparation chamber attached directly to the AEM. Because the surface layer of the thin foil specimen represents a significant proportion of the foil thickness, surface analysis preparation techniques now used for Auger, XPS and other surface analysis techniques will need to be employed. These sample preparation techniques will, however, enable the investigator to employ surface analysis techniques on the same specimens prepared for AEM, perhaps even in the same instrument.

ELECTRON BEAM DAMAGE

The ultimate limitation to microanalysis in the AEM is beam damage. In the AEM, particularly in 300 to 400 kV instruments, knock-on damage or sputtering effects can occur which may change the local chemistry of the specimen. Voltages for knock-on damage of most elements are well known and surface atom sputtering has been studied (Zaluzec and Mansfield, 1987). In either case, the obvious solution is to operate below the critical threshold voltages, although this will remove many of the attractive aspects of operating at the highest available voltage. Nevertheless, in the future the analyst must consider that we are rapidly approaching the limits of the technique in terms of the ability of the sample to remain unchanged in the microscope.

QUANTIFICATION AND LIGHT ELEMENT ANALYSIS

In order to obtain precision and accuracy approaching 1% rel. in thin film x-ray microanalysis, as obtained in the EPMA, it will be necessary to measure k_{AB} factors to within 1% rel. This goal can only be achieved when x-ray counting statistics approach those available with the EPMA. The further development of high brightness FEG instruments will provide higher electron current in the focused probe. Coupled with more stable instruments, the ability to measure beam current during analysis, and the use of more than one EDS detector, it should be possible to obtain enough x-ray counts to approach 1% counting statistics.

The optimistic outlook for x-ray microanalysis at the 1% accuracy level must be tempered when considering x-ray analysis for the light elements, that is elements with characteristic x-ray lines with energies less than 1.5 keV. The relatively poor resolution of the EDS detector produces peak overlaps from more than one light element or even worse, from the overlap of L lines of heavier elements such as Ti, Cr, Fe, Ni, Cu, etc. As shown by Westwood, et al. (1992), measurements of k_{AB} factors of the light elements approaching the 10% accuracy level are now available. However x-ray microanalysis for the light elements in the AEM will require further development before 1% rel. accuracy can be approached.

WDS POSSIBILITIES

The advantages of the wavelength dispersive spectrometer, WDS, are high-energy resolution (<40 eV), high peak-to-background ratios (over 10 x greater than the EDS), high input (output) count rates (up to 50,000 cps) and the ability to detect and measure the light elements more efficiently than EDS. The addition of a WDS detector to the AEM would improve MMF and the analysis of the light elements and the overlap of characteristic x-ray peaks in the EDS. The disadvantage of the

WDS is the low x-ray flux into the detector ($\sim 10^2$ to 10^3 worse than the EDS) due to the large size of the spectrometer.

Goldstein, et al., (1989) have proposed the addition of a small horizontal WDS unit to the AEM. In this unit the analyzing crystal of the WDS is brought as close to the specimen as for the EDS detector (1 to 2 cm). A design is proposed in which crystal and detector are moved independently by computer-controlled mechanical motors placed within the vacuum of the AEM. Alternate WDS designs are now being developed, which will ultimately help to improve MMF in the instrument, resolve peak overlaps, and detect the light elements without interferences from the L lines of the transition elements.

INSTRUMENT DEVELOPMENT

From the standpoint of x-ray microanalysis, the AEM is still in the development stage. At the present time, it is not an instrument optimized for microanalysis. Using well developed EPMA concepts, a true "electron-probe-nano-analyzer" will undoubtedly be available in the near future. The instrument improvements necessary for an optimized instrument include 1) electron source stability, 2) in-situ probe-current measurement, 3) multi-specimen capability, 4) high detector take-off and collection angle, 5) maximum peak to background ratio and minimum hole count, 6) stage stability and computerized stage control, and 7) ultra high vacuum stage environment and sample preparation assembly (Williams and Goldstein, 1991).

X-RAY IMAGING

This aspect holds great promise for the future. The ability to store the entire EDS spectrum at each pixel in a digital STEM image removes many of the barriers to complete materials characterization. With on line probe current measurements, high voltage FEG AEM instruments, high detector take-off angle and collection angle and enhanced stage stability, it should be possible to take > 10 hour digital scans, and be able to obtain quantitative analyses at each pixel. Typical storage requirements for digital spectrum imaging are in the range from 4 MB to 1 GB and require significant processing time.

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